ASSESSMENT OF NATURAL RADIONUCLIDES ACTIVITY AND HEAVY METALS CONCENTRATION IN PADDY PLANTS AND THEIR INFLUENCING FACTORS IN PENANG, MALAYSIA

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by

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
AEDE	Annual Effective Dose Equivalent
APHA	American Public Health Association
BDL	Below Detection Limit
CCREM	Canadian Council of Resource and Environment Ministers
CEC	Cation Exchange Capacity
DHHS	Department of Health and Human Services
DOA	Department of Agriculture
DR	Dose Rate
EC	Electrical Conductivity
EPA	Environmental Protection Agency
EQA	Environmental Quality Act
FAO	Food and Agriculture Organization
GPS	Global Positioning System
GRS	Gamma Ray Spectrometer
HI	Hazard Index
HPGe	High-Purity Germanium
HQ	Hazard Quotient
IAEA	International Atomic Energy Agency
IARC	International Agency for Research on Cancer
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
ICRP	International Commission on Radiological Protection
MDA	Minimum Detectable Activity
NAA	Neutron Activation Analysis

NaI(Tl)	Sodium Iodide Doped with Thallium
ND	Not Detected
NORM	Naturally Occurring Radioactive Materials
OECD	Organization for Economic Cooperation and Development
OM	Organic Matter
RfD	Reference Dose
TF	Transfer Factor
UNSCEAR	United Nations Scientific Committee on the Effects of Atomic Radiation
UPW	Ultra-Pure Water
USDA	United States Department of Agriculture
WHO	World Health Organization

LIST OF SYMBOLS

α	Alpha particle
β^-	Beta particle
β^+	Positron
γ	Gamma-ray
λ	Decay constant
ρ	Density
ε	Efficiency
μ_m	Mass attenuation coefficient
$A_\circ$	Activity of standard at manufacturing time
A_t	Activity of standard at time of experiment
B_w	Body weight
C_A	Activity concentration
C_{hev}	Concentration of heavy metal
D_{ing}	Ingestion effective dose
DI_{hev}	Daily intake of heavy metal
F_c	Self-attenuation correction factor for energy (E)
F_{ing}	Dose conversion factor for direct ingestion of radionuclide
H_{ex}	External hazard index caused by natural radionuclides
H_{in}	Internal hazard index caused by natural radionuclides
I_A	Annual intake of food
I_D	Daily intake of food
M	Mass of sample
N_b	Background count under a photopeak
N_s	Sample count under a photopeak

N_t	Total count under a photopeak
P_γ	Gamma emission probability
Ra_{eq}	Radium equivalent activity
T	Time period for counting
$t_{1/2}$	Half-life
t_d	Decay time
X_d	Exposure duration for heavy metal
X_f	Exposure frequency for heavy metal
X_t	Mean exposure time for non-carcinogenic effects

PENILAIAN AKTIVITI RADIONUKLID TABII

DAN KEPEKATAN LOGAM BERAT DALAM POKOK PADI

DAN FAKTOR PENGARUHNYA DI PULAU PINANG, MALAYSIA

ABSTRAK

Kajian ini memfokuskan mengenai pengukuran keradioaktifan tabii dan logam berat dalam beras (*Oryza sativa*) dan medium di sekitarnya, termasuklah tanih pertanian dan air pengairan. Dalam usaha untuk menentukan penyerapan logam ini oleh beras, penggunaan baja dan ciri-ciri fiziko-kimia tanih, seperti pH, keupayaan pertukaran kation, kekonduksian elektrik, bahan organik, dan tekstur tanih juga telah dikaji. Beras dan sampel tanih diperoleh daripada 23 kawasan yang berlainan di Pulau Pinang, dan spesimen air telah diambil dari sungai utama di kawasan kajian. Kajian makmal telah dilakukan ke atas 3 jenis baja yang lazim digunakan dalam penanaman padi dan pengambilan ^{226}Ra, ^{232}Th dan ^{40}K oleh bijirin beras menggunakan penumbuhan padi di dalam pasu pada 3 peringkat pertumbuhan. Aktiviti ^{226}Ra, ^{232}Th dan ^{40}K dalam air, beras dan sampel tanih sepadan telah dianalisis menggunakan spektroskopi sinar gama (HPGe). Kehadiran Cd, Cr, Cu, Fe, Mn, Ni, Pb dan Zn dalam beras dan sampel tanih telah dikaji menggunakan spektroskopi penyerapan atom (AAS). Manakala, kepekatan logam ini dalam sampel air telah diperiksa menggunakan spektroskopi pancaran optik plasma terganding induktif (ICP-OES). Aktiviti ^{226}Ra, ^{232}Th dan ^{40}K dalam tanih padi adalah masing-masing 83.85, 108.11 dan 403.76 Bq kg^{-1}. Kepekatan purata ^{226}Ra dan ^{232}Th adalah lebih tinggi berbanding purata global (masing-masing 32 dan 45 Bq kg^{-1}). Manakala, untuk ^{40}K, nilainya adalah lebih rendah berbanding nilai purata dunia (420 Bq kg^{-1}). Walau bagaimanapun, nilai min radionuklid ini adalah selaras dengan julat nilai

kepekatan sebelum ini di Malaysia. Dalam tanaman beras, kepekatan min ^{226}Ra dalam akar, jerami, sekam dan bijirin adalah masing-masing 7.80, 5.04, 2.32 dan 1.42 Bq kg^{-1}. Nilai yang bersepadan dengan ^{232}Th adalah masing-masing 6.88, 2.91, 1.35 dan 1.03 Bq kg^{-1} dan bagi ^{40}K nilai adalah 147.38, 640.79, 228.58 dan 72.15 Bq kg^{-1}. Aktiviti ^{226}Ra dan ^{232}Th direkodkan sebagai 47% dan 57% di dalam akar dan 9% dan 8% telah tersebar antara bijirin. Kepekatan ^{40}K dalam jerami dan bijirin adalah masing-masing lebih kurang 59% dan 7%. Oleh itu, pengambilan radionuklid tertentu adalah bergantung kepada bahagian tumbuhan, menunjukkan mobiliti dan akumulasi radionuklid pada setiap bahagian tumbuhan tu. Faktor pemindahan (TF_S) beras dari tanih kepada bijirin untuk ^{226}R, ^{232}Th dan ^{40}K adalah masing-masing 1.87×10^{-2}, masing-masing 0.97×10^{-2} dan 2.35×10^{-1}. Kepekatan purata ^{226}Ra dalam air sungai untuk Sungai Muda, Sungai Jarak, Sungai Kerian dan Sungai Kongsi adalah masing-masing 1.23, 2.13, 0.84 dan 1.34 Bq L^{-1}. Nilai untuk ^{232}Th adalah masing-masing 1.01, 1.21, 0.62 dan 0.70 Bq L^{-1}. Manakala, nilai untuk ^{40}K adalah masing-masing 62.87, 75.30, 54.96 dan 41.53 Bq L^{-1}. Oleh itu, air dari sungai-sungai ini adalah secara radiologinya adalah selamat untuk keperluan pertanian dan rumah. Hasil daripada eksperimen menggunakan pasu menunjukkan bahawa pengambilan ^{226}Ra, ^{232}Th dan ^{40}K oleh bijiri beras telah dipengaruhi oleh kepekatan baja yang berbeza dan masa aplikasinya. Kepekatan Cd, Cr, Cu, Fe, Mn, Ni, Pb dan Zn dalam tanih padi adalah masing-masing 0.171, 6.766, 5.336, 7988.19, 3.318, 0.976, 1.787 dan 41.656 mg kg^{-1}. Oleh itu, majoriti sampel tanih mengandungi logam berat di bawah had maksimum yang dibenarkan yang ditetapkan oleh Standard Kualiti Alam Sekitar untuk tanih di Malaysia. Walau bagaimanapun, kawasan kajian telah dicemari dengan Cr, Mn dan Zn masing-masing 13%, 22% dan 39%. Dalam bijirin beras, nilai yang berkaitan logam berat

adalah masing-masing 0.030, 0.292, 0.642, 31.876, 1.026, 0.073, 0.091 dan 19.492 mg kg^{-1}. Walau bagaimanapun, had atas yang dibenarkan untuk Cr, Mn dan Zn dalam beberapa kawasan kajian adalah tidak signifikan kerana kepekatan logam tersebut dalam beras tidak menaikkan dos oral rujukan (RfDs). Faktor pemindahan (TF_S) beras dari tanih kepada bijirin untuk logam berat tersebut adalah masing-masing 0.186, 0.054, 0.242, 0.004, 0.349, 0.082, 0.075, 0,643. Kepekatan Cr, Fe, Pb, Cd, Cu, Ni dan Zn dalam air sungai adalah masing-masing berada dalam julat 2.0 -3.0, 11.0 - 549.0, 12.5 - 52.0, 1.0 - 1.7, 4.0 - 6.3, ND - 30.3 dan ND - 28.3 μg L^{-1}. Walau bagaimanapun, Mn tidak dikesan dalam mana-mana spesimen. Selain daripada kepekatan Pb di Sungai Kerian, semua kepekatan logam berat tersebut berada dalam julat yang dibenarkan seperti yang ditetapkan oleh Piawaian Kualiti Air Malaysia.

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ABSTRACT

This research focus on the measurement of natural radioactivity and heavy metals in rice (*Oryza sativa*) and its surrounding media, which include agriculture soil and irrigation water. In order to determine the absorption of these metals by rice, the usage of fertilizers and the physico-chemical features of soil, such as pH, cation exchange capacity, electrical conductivity, organic matter, and soil texture were also studied. Rice and soil samples were acquired from 23 different areas in Penang, and the water specimens were retrieved from the main rivers of the study area. Laboratory studies were performed on 3 common fertilizers and uptake of ^{226}Ra, ^{232}Th and ^{40}K by rice grain using potted plants at 3 growth stages. The activities of ^{226}Ra, ^{232}Th and ^{40}K in the water, rice and corresponding soil samples were analyzed by gamma-ray spectroscopy (HPGe). The presence of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the rice and soil samples were investigated by atomic absorption spectroscopy (AAS), whereas the concentration of these metals in water samples were examined by inductively coupled plasma optical emission spectroscopy (ICP-OES). The activities of ^{226}Ra, ^{232}Th and ^{40}K in paddy soil were 83.85, 108.11 and 403.76 Bq kg^{-1}, respectively. The average ^{226}Ra and ^{232}Th concentrations were higher than the global average (32 and 45 Bq kg^{-1}, respectively), whereas that of ^{40}K was lower than the world average (420 Bq kg^{-1}). However, the mean values of these radionuclides were consistent with the prior ranges of concentration in Malaysia. In the rice plant, the mean concentrations of ^{226}Ra in root, straw, husk

and grain were 7.80, 5.04, 2.32 and 1.42 Bq kg^{-1}, respectively. The corresponding values of ^{232}Th were 6.88, 2.91, 1.35 and 1.03 Bq kg^{-1}, whereas the ^{40}K values were 147.38, 640.79, 228.58 and 72.15 Bq kg^{-1}, respectively. ^{226}Ra and ^{232}Th activities were recorded as 47% and 57% in the roots and 9% and 8% were dispersed among the grains. The concentrations of ^{40}K in the straws and grains were approximately 59% and 7%, respectively. Thus, the uptake of the particular radionuclides depended on plant compartments, reflecting their mobility and accumulation in each part. Rice soil-grain TFs were found to be 1.87×10^{-2}, 0.97×10^{-2} and 2.35×10^{-1} for ^{226}R, ^{232}Th and ^{40}K, respectively. The average concentrations of ^{226}Ra in river water for Sungai Muda, Sungai Jarak, Sungai Kerian and Sungai Kongsi were 1.23, 2.13, 0.84 and 1.34 Bq L^{-1}, respectively. The respective values of ^{232}Th were 1.01, 1.21, 0.62 and 0.70 Bq L^{-1}. The values of ^{40}K were 62.87, 75.30, 54.96 and 41.53 Bq L^{-1}, respectively. Thus, water from these rivers is radiologically safe for household and agricultural purposes. The results from pot experiments showed that the uptake of ^{226}Ra, ^{232}Th and ^{40}K by rice grains was affected by the different concentrations of fertilizer and its application time. The concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in paddy soil were 0.171, 6.766, 5.336, 7988.19, 3.318, 0.976, 1.787 and 41.656 mg kg^{-1}, respectively. Thus, the majority of the soil samples contained heavy metals under the maximum permissible limit set by the Environmental Quality Standard for Soils in Malaysia. Nevertheless, 13%, 22% and 39% of the study area were correspondingly tainted with Cr, Mn and Zn. The associated values of the metals in rice grain were 0.030, 0.292, 0.642, 31.876, 1.026, 0.073, 0.091 and 19.492 mg kg^{-1}, respectively. However, the upper limits of Cr, Mn and Zn in the study areas were insignificant because their concentrations in rice did not raise oral reference doses (RfDs) of these metals. Rice soil-grain TFs of aforementioned heavy

metals were found to be 0.186, 0.054, 0.242, 0.004, 0.349, 0.082, 0.075 and 0.643, respectively. The concentrations of Cr, Fe, Pb, Cd, Cu, Ni and Zn in the river water were 2.0 - 3.0, 11.0 - 549.0, 12.5 - 52.0, 1.0 - 1.7, 4.0 - 6.3, ND - 30.3 and ND - 28.3 μg L^{-1} range, respectively. However, Mn was not detected in any specimen. Apart from the Pb concentration in Sungai Kerian, all concentrations were within the permissible range as determined by Malaysian Water Quality Standards.

CHAPTER 1

INTRODUCTION

1.1 Background

The presence of naturally occurring radioactive elements is universal, ranging from our atmosphere to the inside of the human beings in the form of naturally occurring radioactive materials (NORM) (Hutchison and Hutchison, 1997). However, the concentration of these materials and the consequential radioactive decay is uneven around the globe depending on the geographical and geological characteristics (Almayahi et al., 2012a; Harb et al., 2012; Dragović et al., 2014). For instance, primitive radioisotopes of ^{226}Ra, ^{232}Th and ^{40}K, even though unevenly distributed around the world, contribute towards the greatest share of external radiation (UNSCEAR, 2000). Amongst these, ^{40}K serves as a nutrient for the human beings even though all three of them are radiotoxic to the human (Atwood, 2013). Taking into consideration the human body, the primary sources of irradiation are gamma radiations emanating from these natural radioactive isotopes, specifically from radionuclides present beneath the earth's surface (UNSCEAR, 2000). Apart from giving rise to cancers and inducing genetic mutations, high doses of gamma radiations can also destroy cells or at least alter their functions. However, the exact relationship between the dose and its effect in case of low doses is still not clear (Cardoso et al., 2011). Anyway, it is crucial to assess the dose of gamma radiations emanating from these aforementioned natural sources since it accounts for the greatest portion of the external dose affecting human population (Mehra, 2009).

Industrialization, population growth, and technological developments have led to a huge increase and accretion of heavy metals in the environment (Liu et al., 2009; Salati and Moore, 2010). Conclusively, the enormous aggregation and deployment of

heavy metals into our atmosphere has mostly been caused by unchecked outflow and release from manufacturing industries, excessive usage of chemical fertilizers, mining, utilization of industrial effluents on sewage and land waste and eventually lead to the contamination of the arable land at a very large scale (Zhao et al., 2010). Cd, Cr, and Pb, classified as heavy metals, are released into the environment mainly through human activities; these metals are highly toxic even at minute quantities. Similarly, other heavy metals including Cu, Fe, and Mn when released into the environment beyond their permitted limits cause destructive alterations to the natural environment; however, these metals are also formed naturally and provide nutrition to plants when present in permissible quantities (Eneji et al., 2012).

The mechanism relating the release of toxic metals to its implication on the human health is as follows: after getting seeped into the arable land, these metals are absorbed by the roots of the plants and eventually spread to other parts of the plant including its fruits and leaves. Internal exposure to human body is caused by the edible parts of the plants being used by human beings (Pulhani et al., 2005). Even though such substances are generally excreted from the human body through kidneys and the digestive system, it is equally possible for these metals to accumulate and deposit inside human organs and bones over a long period of time. Eventually, these accumulations have the tendency to cause various fatal disorders and diseases with kidneys and the brain cells being most affected by the toxicity of these metals (Hu, 2002). Therefore, it is extremely crucial that the likely spread of these aforementioned heavy metals and radionuclides is checked which may assist in the provision of effective utilization of herbicides, inorganic and organic fertilizers and pesticides which could lead to healthy crops and eventually prevent various health related issues.

Yet another consequence of industrialization coupled with other human activities, including discharge of wastage into the water bodies, have resulted in severe water pollution which has proven to be a grave environmental issue having a detrimental effect on both marine and human life (Alkarkhi et al., 2008). Even though natural causes, including erosion of rocks and soils, also cause discharge of metals into the water bodies, studies have shown a positive correlation between industrialization and increased levels of heavy metals in the aquatic atmosphere (Guerrero and Kesten, 1994; Ayenimo et al., 2005). Moreover, the favourable chemical and physical properties of water including salinity, pH level and temperature also impact the solubility and ultimate accumulation of the aforementioned heavy metals into the aquatic environment (Barlas et al., 2005).

International authorities, such as World Health Organization monitors the maximum permissible quantities of the toxic metals into water bodies and edible substances to guarantee their safety (WHO, 1995). This is due to the fact that the utilization of contaminated water for crops have increased the concentration of heavy metals in the agricultural soil, leading to enhanced levels of soil pollution (Bhaskar et al., 2010). This could eventually lead to enhanced concentrations of these metals in human bodies through the increased levels in edible crops (Malan et al., 2015). Therefore, to combat the hazard of metal toxicity in human beings, the quality of the river water is also being monitored since it can be used for drinking purposes directly by humans, or could end up in their bodies through the food chain.

In order to examine the transfer of toxic metals through food chains, the mean figures for soil-plant transfer factor (TF) are utilized which are considered to be the primary evaluation methodology examining the link between food intake and presence of radioactive isotopes and heavy metals in human bodies (IAEA, 2010).

The isotope-binding methodology of the soil along with the particular type of plant determines the TF. Still TF may fluctuate depending upon the site, time passed after contamination and season (Martinez-Aguirre and Perianez, 1998). Therefore, the fact that needs to be taken into consideration is that TF is location specific and specific data should be utilized every place. Along with these factors, the absorption and adsorption of the metals is also dependent upon the characteristics of the soil including organic matter (OM), cation exchange capacity (CEC), clay mineral contents, electrical conductivity (EC) and the pH (Nadimi-Goki et al., 2014).

Even though fertilizers are widely and commonly utilized to improve the crop yield by providing required nutrients to the soil, they also serve to disturb the natural characteristics of the soil by altering the biological, physical and chemical characteristics (Zhong and Cai, 2007). For instance, the utilization of chemical fertilizers alone was not very successful in maintaining high crop yield due to their impact on the organic matter, nutrient leaching along with pH of the soil (Obi and Ebo, 1995). Furthermore, the presence of phosphate compounds also makes fertilizers detrimental to the soil since phosphate is known to contain different amounts of thorium and uranium along with their radioactive decay products which could eventually lead to increase of natural radionuclides and hence increasing the dose to which the consumers are exposed (Cardoso et al., 2011). Therefore, further research into the subject of the impact of fertilizers on the presence of heavy metals and radionuclides is required to establish such a relationship.

One of the primary economic crops of Malaysia is rice which has increased its consumption to almost 96 kg per adult annually (USDA, 2013), with about 72% produced locally and the rest is imported from abroad (DOA, 2012). Malaysia is presently undergoing rapid industrial development and there have been incidences of

toxic pollution from industry (Alkarkhi et al., 2008). One of the main areas for planting rice in Malaysia is Penang (DOA, 2012) which also happens to be the most developed, populated and urbanized (Marcinkowski, 2012). Contaminations resulting from natural radioactivity in crops (including tomato, eggplant, lattice, pumpkin, cucumber, onion, okra, and chilli) and agricultural soil in Penang have already been examined in studies performed before (Aswood et al., 2013). Similarly, in Bumbung Lima (Jamil et al., 2013) and Kampung Permatang Tok Labu (Asaduzzaman et al., 2015), toxic metals in the paddy soil along with the presence of contaminations in the river of Sungai Juru (Idriss and Ahmad, 2013) were also examined. For further investigation, these researches aim to find out the overall levels of contamination resulting from the aforementioned heavy metals and radioisotopes in paddy soil, irrigation water and rice in the region of Penang, Malaysia to quantify the various routes of human toxicity along with their combined impacts.

1.2 Problem Statement

The environment can be polluted by heavy or radiotoxic metals due to increased industrialization and other human pursuits, in addition to naturally occurring radioactive materials (NORM). The soil composition and texture are also affected by an increased use of fertilizers which in turn affects the uptake of these metals by the plants. The consumption of plants affected by the deposition of such metals is harmful for humans and can lead to various serious health concerns.

With a plantation area of 12,782 ha, the Penang fields have an estimated paddy yield of 5913 kg ha^{-1} (DOA, 2012). Due to extreme usage of land resources and high industrialization in the Penang region, the water bodies on Penang coasts have a

greater concentration of heavy metals than those of other water bodies in Peninsular Malaysia (Ahmad et al., 2003; Alkarkhi et al., 2008). Therefore, the concentration and discharge of heavy elements coupled with presence of natural radioactivity in soil, water, and rice provide us very important information regarding the monitoring of the environmental contamination along with the adverse effects on the health of the regional population.

1.3 Objectives of the Study

The objectives of the research are as follows:

a. To quantify the levels of natural radioactivity and heavy metals in water, rice and soil.
b. To estimate the external hazard that occurs as a result of the natural radioactivity and heavy metals in paddy soil and water employed for agricultural purposes along with the assessment of the internal hazard caused by consumption of rice by the locals.
c. To determine the transfer factors (TFs) for both natural radionuclides and heavy metals from soil to paddy grain (rice).
d. To estimate the link between the utilization of fertilizers and the intake of radioactive elements by the rice crop along with the effect of the soil characteristics on the TFs.

1.4 Scope of the Study

The study to be conducted will evaluate the level of natural radioactivity (^{226}Ra, ^{232}Th and ^{40}K) and heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) presence in samples of paddy soil, irrigation water, and rice (*Oryza sativa*) in

Penang, Malaysia. Rice samples will be obtained from different paddy areas in Penang and the water specimens will be collected from the main rivers of the area. The study will include the uptake of such materials by plants and how it is affected by fertilizers. This study is significant as it provides a baseline data for the accumulation of heavy metals and natural radioactivity in the water, soil and rice in the study area.

1.5 Thesis Outline

Chapter 1 provides some background of natural radioactivity and heavy metals in soil, plant and aquatic bodies along with outlining the objectives and significance of the study. Chapter 2 provides basic knowledge along with review of the concerned literature regarding radioactive isotopes and heavy metals in soil, plant and irrigation water along with outlining the hazard attached when inducted into humans. Chapter 3 outlines the area utilized for the study, preparations of the sample, explanations of the equipment used, the instruments used and their calibrations, the set-up for the experiment, and the procedure utilized for analysis. Chapter 4 enlists the results of the paddy soil, rice and water content including the heavy metals and natural radioactivity. It also elaborates on the hazard caused to the local population along with the distribution of the radioactive isotopes in rice plants, the effect of transfer of the isotopes from soil to rice depending on the characteristics of the soil and finally the effect of fertilizers on the intake of these isotopes. Chapter 5 concludes the study along with the provision of the final results, recommendations and any future endeavours.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Radioactivity

Naturally, world is radioactive and natural sources, like cosmic, terrestrial, and contact with radiation give rise to around 82% of human-absorbed radiations, which are uncontrollable (Shahbazi-Gahrouei et al., 2013). Radioactivity with respect to cosmic radiation emerges from two kinds of particles: the primary active particles like, electrons, protons, alpha etc., from extra-terrestrial that strike the atmosphere; and the secondary particles or cosmogenic radionuclides, like ^{3}H, ^{7}Be,^{14}C ,^{22}Na etc., which are constantly created when active particles from these cosmic rays strike the atmosphere (Cember and Johnson, 2009). The earth and its atmosphere is made up of radionuclides that are present in air, soil, water and rocks, through several factors they can move to ecosphere and added in food (Eral et al., 2003). On regular basis human beings come in contact with great amount of radioactivity that originates from surroundings. NORM, the naturally occurring radioactive material, consists of isotopes that subsist on its own or are constituents of the basic radioactive decay series that cause exposure to radiation for human environment (Eisenbud and Gesell, 1997). The major external cause of irradiation of the human body exists in the earth's crust; it includes uranium and thorium series, as well as ^{40}K radionuclide (Al-Trabulsy et al., 2011). Due to tremendous amount of radioactivity present in soil some parts of the earth naturally have higher radioactive levels; however the radioactive levels at majority of the places are comparable (Esposito et al., 2002). Various global researches have been conducted in the past several years that have revealed distinctive values with respect to the impact of background radiation on the health of humans (Almayahi et al., 2012b). Human beings cannot change their

exposure to the natural sources, cosmic rays and natural radioactivity within the bodies (Friedberg et al., 1993). However, the fundamental requirements and points of confinement for the assurance of health and the earth from ionizing radiation has been determined by the international basic safety standards for protection against ionizing radiation and the safety of radiation sources (IAEA, 1996).

Primordial radionuclides, such as ^{238}U, ^{232}Th, as well as their daughter nuclides in the decay series, and ^{40}K are present in varying degrees in soil, water, air and in living organisms. As a result, human beings are exposed to external and internal irradiations by gamma-rays, beta particles and alpha particles with varying ranges of energies (IAEA, 1989). Moreover, the chemical structure (speciation) and the intake characterize the health effects of any metal. Therefore, it is imperative to have an advanced evaluation regarding the transfer of uranium, thorium or potassium from geo-to bio-system and dissemination in the bio-system as well as the information related to the physical and chemical behavior of these metals (Bernhard, 2005).

2.1.1 Uranium

The actinide group has a dense grey-silver metallic element, with an atomic number of 92 and an atomic mass of 238.03 known as uranium (U). In the environment the natural background radiation of low intensity are cause of uranium and its decay products. It has been found that the availability of uranium in the Earth's crust is not as scarce as it was known with and average concentration of 2.7 ppm, which in fact is more than mercury, silver, or cadmium. Minerals like, pitchblende, uraninite, carnotite, and autunite also contains uranium. Moreover, uranium can be commercially extracted from phosphate rock, lignite, and monazite sands.

Natural uranium occurs as three radioactive isotopes, ^{238}U, ^{235}U and ^{234}U, with respective abundance of 99.27%, 0.72% and 0.0055% and half-lives of 4.47×10^9, 7.04×10^8 and 2.46×10^5 years. Uranium is highly radiotoxic because of its long half-life. Natural uranium has a 25 Bq mg^{-1} specific activity. A chain of several other radioisotopes of the natural uranium atoms of ^{238}U and ^{235}U decay so that the lead isotopes can be settled (Atwood, 2013). Through α-emission ^{238}U isotope decays to ^{234}Th that formulates protactinium-234 (^{234}Pa) by due to β-decay. This reaction involves 14 nuclear decay steps resulting in the emission of eight α-particles and six β-particles. The ^{238}U and ^{234}U belong to one family called the uranium series (4n+2). The divisibility of the mass numbers of respective series by 4n+2 provides the credential numbers. The ^{235}U isotope belongs to another series called the actinium series (4n+3) (Cember and Johnson, 2009). The decay schemes for primordial ^{238}U and ^{235}U are demonstrated in Figures 2.1 and 2.2, respectively (Poschl and Nollet, 2006).

The natural isotopes that are decay products of the ^{238}U and ^{232}Th radioactive series that can also affect the ecological system are ^{226}Ra with a half-life of 1600 years, and ^{228}Ra with a half-life of 5.7 years, respectively. The early account of radium's discovery is closely linked with the primary researches on radioactivity; also both isotopes of radium are radioactive with the atomic number 88. Due to high radiotoxicity the occurrence of radium in environment is dangerous, although it is present in very small quantity. Therefore, the emphasis has been put on human health by estimating its activity through soil and water (Atwood, 2013).

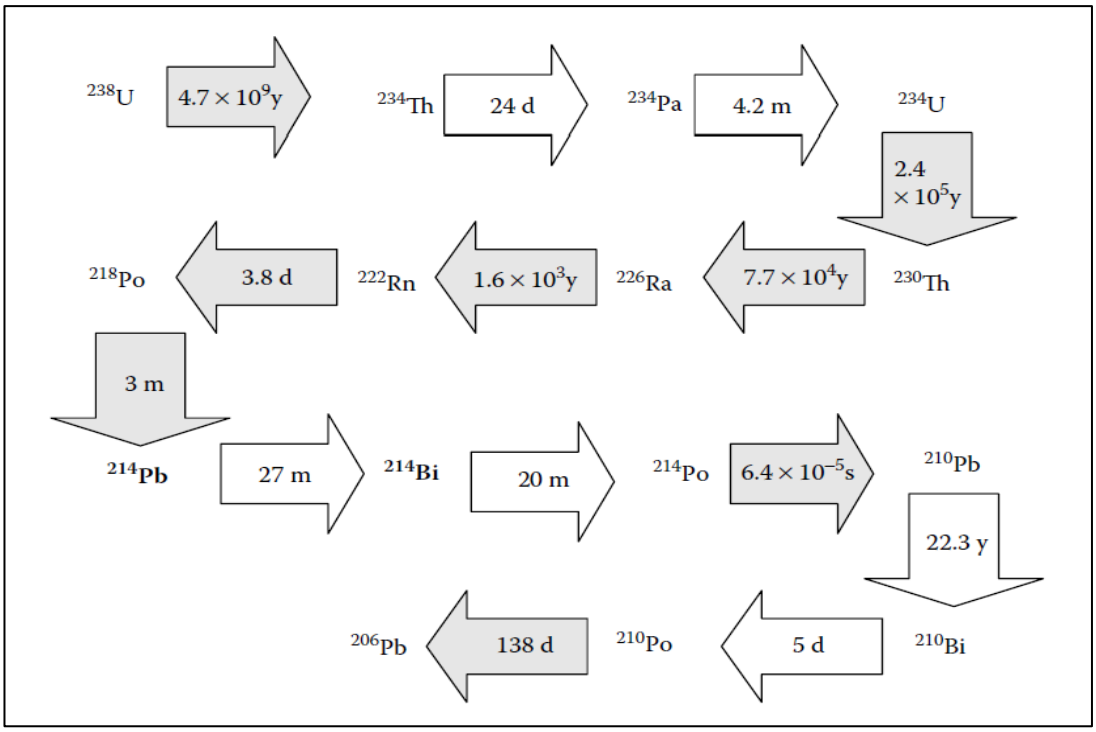

Figure 2.1: Uranium (^{238}U) decay series (4n + 2)

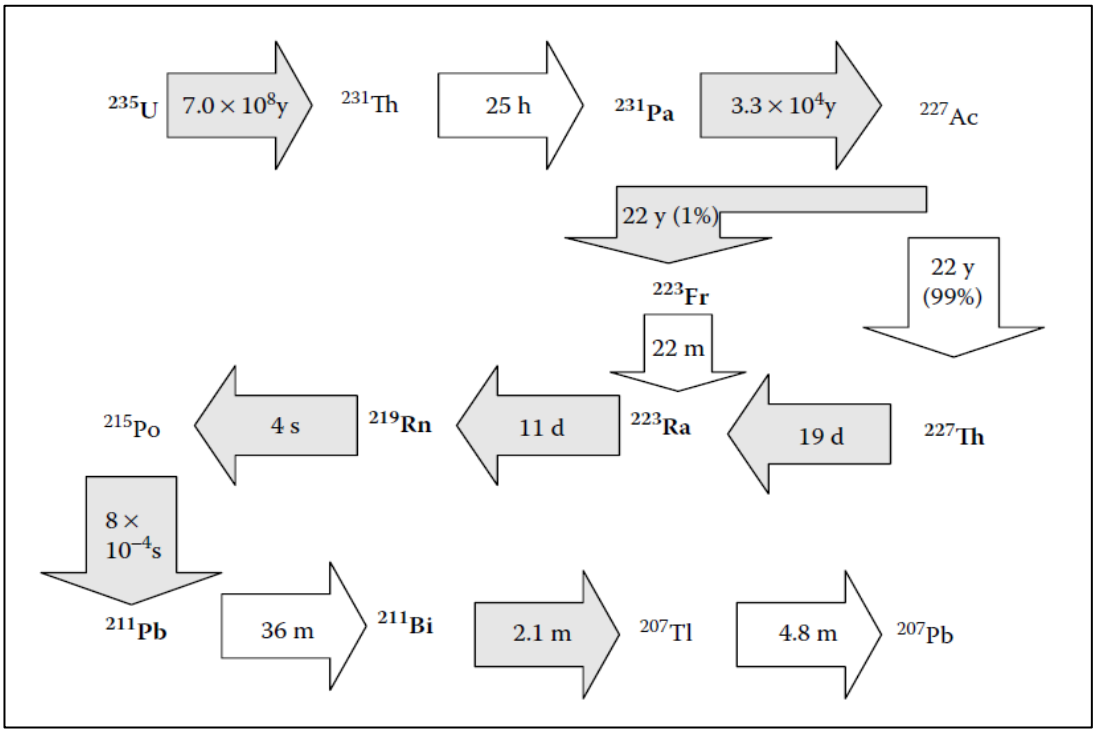

Figure 2.2: Actinium (^{235}U) decay series (4n+3)

^{226}Ra and ^{238}U are usually in balance in natural undisturbed soil, while they may not be in balance in disturbed soil. In natural undisturbed environments, the presence of natural radionuclides is in the form of secular equilibrium. The radiological secular equilibrium for each series may be unstable because of physico-chemical courses in the earth's crust, like leaching and emanation (Cember and Johnson, 2009).

2.1.2 Thorium

As a whole, naturally and/or artificially thorium (Th) has 25 radioisotopes. The nuclear properties of thorium isotopes may differ as well as their half-lives of seconds to 10^{10} years. The atomic number of these isotopes is 90 and the atomic mass is from 212 to 236, and under all redox situation in natural water the constant oxidation state is (+4) (Santschi et al., 2006). Naturally, there are six thorium isotopes: with β-emitting ^{234}Th (24.10 days) and α-emitting ^{230}Th (7.54×10^4 y) in uranium (^{238}U) series; α-emitting ^{232}Th (1.41×10^{10} y) and ^{228}Th (1.913 y) in thorium (^{232}Th) series; and β-emitting ^{231}Th (25.52 h) and α-emitting ^{227}Th (18.72 days) in ^{235}U series.

As ^{232}Th has comparatively longer half-lives, higher natural abundance or activity concentration it is of more significance (Jia et al., 2008). Due to its decay into a series of other α-, β-, and/or γ- emitting progenies ^{232}Th is known as one of the highly radiotoxic elements (Talip et al., 2009). ^{232}Th is the first member of a long series called the thorium series (4n) (Cember and Johnson, 2009). Thorium (^{232}Th) decay series has been demonstrated in Figure 2.3 (Poschl and Nollet, 2006).

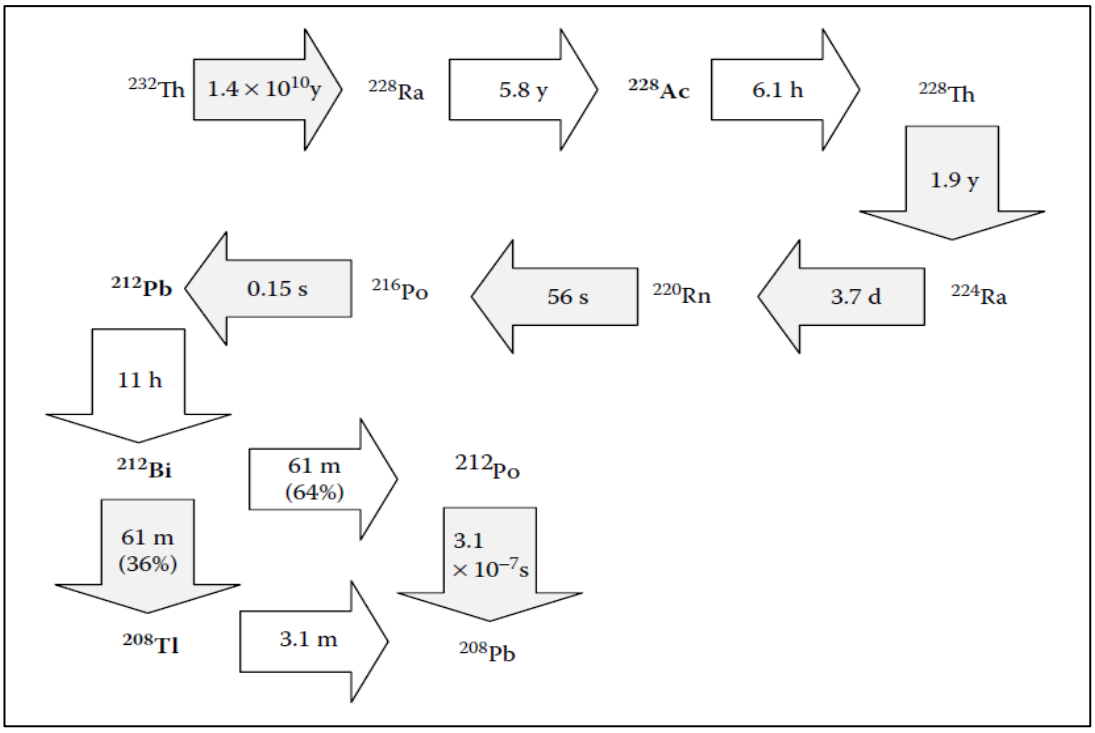

Figure 2.3: Thorium (^{232}Th) decay series (4n)

In earth's crust, the distribution of thorium is generally spread in small quantities with an average lithospheric concentration of 8 - 12 mg g^{-1}, at an average concentration of 6 mg g^{-1} in soil. So, in quantity it is approximately twice as much as uranium (Jia et al., 2008). Its concentration is only a few parts per million (ppm) in sedimentary rocks, whereas it can be 10 times higher in acid igneous rocks (Atwood, 2013). Appendix A - Tables A1, A2 and A3 provide the decay modes and their energies for ^{238}U, ^{235}U and ^{232}Th series, respectively (IAEA, 1989; Wahl, 2007).

2.1.3 Potassium

A soft silvery-white alkali metal that can be easily oxidized in air to its (+1) recognized oxidation state is potassium (K). Potassium is a simple cation (K^+) that is present in several preparations as a positive counterion in minerals and is pervasive in biology. It is highly reactive with water and is also a vital part of human body by

controlling the electrical system, with the assistance of Na^+ to regulate water in the body.

There are total 28 known isotopes of potassium, among which only three are natural: ^{39}K (93.3%); ^{40}K (0.012%) (terrestrially important); and ^{41}K (6.7%). The element is of great significance with respect to natural radiation due to the half-life of ^{40}K as 1.28×10^9 years (Atwood, 2013). Figure 2.4 demonstrates the natural ^{40}K decays to stable ^{40}Ar (10.75%) by electron capture and by positron emission, and decays to stable ^{40}Ca (89.25%) by beta emission. For every 100 disintegration happen in this decay process, around 11 of which emit gamma photons with maximum energy of 1.46 MeV and 89 of them emit beta particles with maximum energy of 1.31 MeV (Vearrier et al., 2009).

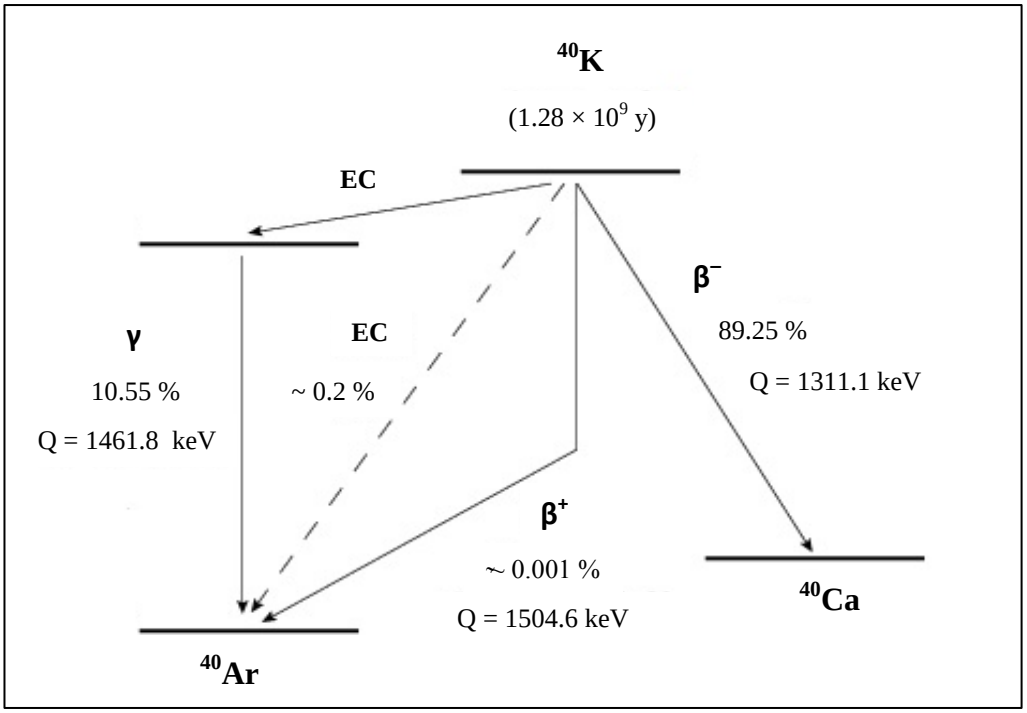

Figure 2.4: Decay scheme of ^{40}K

Natural potassium has the activity of 31 Bq g^{-1}. ^{40}K characterizes the major source of radioactivity in healthy animals and people, even more than ^{14}C. A 70 kg mass of human body undergoes about 4,400 nuclei of ^{40}K decay every second (Knoll, 2010). However, potassium content in the body is under homeostatic control and is scarcely affected by the ecological changes and as a result the dose from ^{40}K in the body is reasonably constant (Vearrier et al., 2009).

2.2 Heavy Metals

Elements that have atomic weights in range of 63.5 and 200.6, and a specific gravity more than 5.0 are called heavy metals. For thousands of years humans have been using heavy metals (Lakherwal, 2014). Majority of these heavy metals are perilous to health and environment. Albeit heavy metals are quite harmful to health, their usage have continued and is in fact increasing every day in some areas of the world; however, from the past century the usage have decreased in majority of the developed countries (Järup, 2003). Major environmental pollutants are trace heavy metals, like Cd, Pb, Cr and Ni; they are more effective in areas that have high anthropogenic pressure. Moreover, Cu, Mn, Fe and Zn are also among the significant trace micronutrients. It is hazardous to every organism to have the existence of trace heavy metals in the atmosphere, soil and water; human health can be affected due to the great deal of bioavailability of heavy metals that can lead to the bioaccumulation in the food chain (Waseem et al., 2014).

2.2.1 Cadmium

Cadmium (Cd) along with Hg and Pb are the greatest heavy metal poisons and is not recognized for any vital biological function. Its atomic number is 48, atomic

weight is 112.4, density is 8.65 g cm^{-3}, melting point is 320.9 °C, and boiling point is 765 °C. Cd exists as the divalent Cd (II) ion in its compounds. In the periodic table, Cd is placed right below Zn which is a vital micronutrient for plants and animals; therefore they both have similar chemical properties. As Zn is an important trace element, it may be the reason of Cd's toxicity; it is possible to disturb the metabolic processes be replacing Zn and Cd (Campbell, 2007).

The total concentration of Cd in soils is increased by the use of agricultural inputs like, agrochemicals, pesticides, and bio solids (sewage sludge), the disposal of industrial wastes or the deposition of atmospheric contaminants and the bioavailability of the Cd determines whether plant Cd uptake occurs to a significant degree (Wuana and Okieimen, 2011). Moreover, several products like phosphate fertilizers, detergents and refined petroleum products have Cd present in them. The geochemical mobility of Cd is increased by acid rain and the subsequent acidification of soils and surface waters, consequently with the decrease in water pH the surface-water concentrations is likely to increase (Campbell, 2007).

2.2.2 Chromium

Chromium (Cr) is the 17th most abundant element in the earth's crust (Oliveira, 2012) and is naturally available as a compound. Cr has the atomic number of 24, atomic mass of 52, density of 7.19 g cm^{-3}, melting point of 1875 °C, and boiling point of 2665 °C (Asrari, 2014). There are numerous oxidation states of Cr but the most common forms: Cr (0), the trivalent Cr (III), and the hexavalent Cr (VI) species. The metallic form Cr (0) is made in industry and is solid with high fusion point commonly employed for making steel and other alloys. The most toxic form of Cr is Cr (VI), in the forms of chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) because it

is highly oxidizing, high solubility, and mobility in the membranes of living organisms and in the environment. The toxicity of Cr (III) in the form of oxides, hydroxides, and sulphates is less because it is comparatively soluble in water and has lower mobility, and is largely bound to organic matter in soil and water systems. Cr (III) can be oxidized to Cr (VI) at high concentrations of oxygen or Mn oxides (Peralta-Videa et al., 2009).

Mobility of Cr is based on sorption features of the soil, as well as clay content, iron oxide content, and the presence of organic matter. In its soluble or precipitated form Cr can be transferred by surface runoff to surface waters. A large portion of Cr discharged into regular waters is molecule related, however, and is eventually stored into the residue (Asrari, 2014).

Sufficient intake of Cr for men and women respectively is 35 and 25 $\mu g\ day^{-1}$ as per the National Institute of Health, Office of Dietary Supplements. Cr is a crucial micronutrient in the human body; it is related to the circulation of countless processes including glucose homeostasis, elevated circulating insulin, and even impair growth can occur due to deficiency of Cr in body (Yin and Phung, 2015).

2.2.3 Copper

The properties of copper (Cu) are: atomic number 29, atomic weight 63.5, density 8.96 $g\ cm^{-3}$, melting point 1083 °C and boiling point 2595 °C. A 55 $mg\ kg^{-1}$ is the copper's average concentration in crustal rocks (Peralta-Videa et al., 2009). Cu is present in soil in large amount but the concentration of Cu is different in each sample based on the parent rock type and proximity to manufactured sources. In organic and mineral soils, Cu can be present from 1 to 200 ppm, as a result of soil pH and soil texture. Cu and soil pH are inversely proportional, the value of one

increases as the other decreases. Moreover, Cu is not mobile in soils and it is attracted to soil organic matter and clay minerals. Cu is a crucial component of proteins in plants, it is found in enzymes that manage the rate of numerous biochemical responses in plants. The growth of plants would not be possible without the availability of these particular enzymes (Cooper et al., 2007).

Cu with small quantities plays an important role in the human body by supporting the proper and efficient functioning of certain enzyme systems, particularly the production of catecholamine. In large quantities, however, Cu can be hazardous for both animals and humans (Eneji et al., 2012). While Cu has an intricate relation with the environment, it has been found from research that in the environment Cu quickly becomes stable and is not dangerous to the environment (Wuana and Okieimen, 2011).

2.2.4 Iron

In the earth crust iron (Fe) is the 4th most profuse element with the atomic weight of 55.85 and a density of 7.68 g cm^{-3}. The characteristic of pure Fe is that it is a white lustrous metal with the melting point of 1528 °C. Ferrous (Fe (II)) and Ferric (Fe (III)) is the two compounds that are created from Fe. It is also present in other oxidation forms but they are not biologically significant. FeO, Fe_2O_3, and Fe_3O_4 are the three oxides that signify the Fe(II) and the Fe(III) and the mixed Fe(II)-Fe(III) oxide, which is naturally present as the mineral magnetite (Reilly, 2008). Fe is discharged naturally into the environment due to the weathering of sulphide ores and igneous, sedimentary and metamorphic rocks and by human activities, such as the burning of coke and coal, acid mine drainage, mineral processing, sewage, landfill leachates and the corrosion of iron and steel (CCREM, 2008). Due to the low

solubility of Fe in water its concentration in marine environment is very low and it usually does not surpass 1 mg L^{-1} (Xing and Liu, 2011).

Every living organism biologically needs Fe to survive. However, regardless of its geologic plenitude, Fe usually prevents growth in the environment; this is because of the fact that when it forms oxides with oxygen it becomes highly insoluble, and thus is not readily available for uptake by organisms (Abbaspour et al., 2014). From the perspective of human biology, the most significant chemical property of Fe is its potential to formulate coordination compounds with organic molecules, specifically the porphyrin nucleus. The most imperative of these are the haem pigments, which can be found in haemoglobin and myoglobin due to which oxygen circulates in the body (Reilly, 2008).

2.2.5 Manganese

Naturally, manganese (Mn) can be found in rocks, soil, water and food, and is the 12th most plentiful element in the earth's crust (Santamaria, 2008). The physical properties of Mn are: atomic number of 25, atomic weight of 54.94, melting point of 1244 °C and a specific gravity of 7.2. Humans, animals and plants require Mn for health, growth and development. The chemical characteristic of Mn is quite comparable to Fe. I, II, III, IV, VI, and VII are the oxidation states of Mn. Metamorphic, sedimentary, and igneous rocks usually contains Mn. In the lithosphere, the average concentration of Mn is 1000 ppm. Among hundreds of Mn minerals like, sulfides, oxides, carbonates, silicates, phosphates, arsenates, tungstate, and borates the native black manganese oxide, pyrolusite (MnO_2) is the most significant of them all (Bradl, 2005). In industry Mn is used for manufacturing of ferromanganese steels and electrolytic manganese dioxide for use in batteries, alloys,

catalysts, pigments, wood preservatives and coating welding rods (Santamaria, 2008).

During the lifetime of all mammals Mn is vital for the normal growth and body function. Approximately 80% of Mn in brain is linked with astrocyte-explicit enzyme glutamine synthetase, where it plays an administrative part, despite the fact that it is not a required co-element (Crossgrove and Zheng, 2004).

2.2.6 Nickel

Nickel (Ni) is an abundantly present trace metal that is introduced into the environment either through anthropogenic activities or natural sources. Only 3% of the earth's crust is Ni, which makes it the 24th most profuse element (Cempel and Nikel, 2006). The properties of Ni are: a silver-white malleable metal, atomic number 28, atomic weight 58.71, density 8.9 g cm^{-3}, melting point 1453 °C, and boiling point 2732 °C (Nordberg et al., 2014). The presence of Ni in the environment is very low as well as its requirement, but large amount of it can be hazardous. Ni pollutes soil through: metal plating industries, combustion of fossil fuels, nickel mining, electroplating. Ni can expose animals, particularly the ones subsisting near refineries, to numerous types of cancers (Khodadoust et al., 2004). In plants, excess Ni affects nutrient absorption by roots, retard shoot and root growth, impairs plant metabolism and decrease biomass production (Ahmad and Ashraf, 2012).

Most ingested Ni is not absorbed and is more likely to be detached from the humans as waste. A portion of the Ni assimilated from the gastrointestinal tract is discharged during urination and is related fundamentally with low sub-atomic weight edifices that contain amino acids (Das et al., 2008).

2.2.7 Lead

Lead (Pb) is a bluish or silvery-grey metal that has following properties: atomic number 82, atomic weight 207.19, and a specific gravity of 11.34, melting point of 327.5 °C and a boiling point of 1740 °C. Naturally, Pb has four isotopes with atomic number in decreasing order of their abundance: 208, 206, 207 and 204. Majority of the inorganic salts of Pb^{2+} except nitrate, chlorate, and chloride are nearly insoluble in water (Tangahu et al., 2011). Around the world, Pb is naturally accessible in a wide range of variety and today it is known to be the among the most generally and uniformly circulated trace metals. Industrial areas, leaded fuels, old lead plumbing pipes, car exhaust, dust, and gases from numerous industrial sources can pollute vegetation and soil with Pb. It is dangerous to plants, animals, and microorganisms; its impacts are usually confined to the polluted regions. Pb is most commonly available in water and if its occurrence exceeds its limits it can be poisonous (Naja and Volesky, 2009).

2.2.8 Zinc

Zinc (Zn) has the following properties: atomic number 30, atomic mass 65.4, density 7.14 $g\,cm^{-3}$, melting point 419.5 °C, and boiling point 906 °C. The presence of Zn in soil is natural; almost 70 $mg\,kg^{-1}$ in crustal rocks (Wuana and Okieimen, 2011), but because of anthropogenic additions concentration of Zn seems to be increasing oddly. Zn is usually accumulated from the industrial activities, such as mining, coal, and waste combustion and steel processing.

Zn is present in some foodstuffs. Due to unnatural presence of Zn in soil, plants usually have higher uptake of Zn than they can manage. Health problems arise due to the presence of Zn in drinking water from the industrial sources or toxic waste

sites. Resultantly, Zn-contaminated slime is consistently dumped by the river banks (Subhashin et al., 2013).

For good health of humans Zn is an important trace element. Among the heavy metals, Zn should have the minimum amount of toxicity. Moreover, the contribution of Zn in the protein synthesis, as in the carbohydrate, nucleic acid and lipid metabolism is very crucial. DNA and RNA combines with Zn to form stable complexes due to which Zn can most probably influence the stability of DNA and RNA (Påhlsson, 1989).

2.3 Natural Radioactivity in Soil

Generally, the contents of ^{226}Ra, ^{232}Th and ^{40}K are used to identify the natural radioactivity of soil samples. As ^{226}Ra and its daughter products generate about 98.5% of the radiological impact of the uranium series the role of ^{238}U and the other ^{226}Ra are usually ignored (Mehra, 2009). The natural radioactivity of the soil is regulated by the mineral structure of the parent product (Navas et al., 2005) and the degree of activity of natural radionuclides is affected by the method of leaching, sorption, sedimentation and weathering and groundwater movement (Dowdall and O'Dea, 2002). The cycling of radionuclides is largely depended upon the soils, and the bioavailability and movement of these radionuclides in biological networks is affected by the physico-chemical properties of the soil (Navas et al., 2005). The above 30 - 45 cm of the earth's surface radiate almost 90% of the quantifiable gamma radiation (Scott and Pain, 2009) and the value of gamma spectroscopy lies principally in the quantity of radioisotopes of ^{226}Ra, ^{232}Th and ^{40}K contained in rocks and soil profiles (Dickson and Scott, 1997).

The geographical arrangement of every lithological divided area is linked with the particular levels of terrestrial ecological radiation, and to the matter of natural radioisotopes present in the rocks from which soils generate in every part (Maxwell et al., 2015). It is possible that the role of parent materials that form the soil type lead to the higher radioactivity in soil samples (Saleh et al., 2013a). For example, comparatively granite generated soil will be more radioactive than the soil originated from other type of rocks (Ramli et al., 2003). In few parts of the world background radiation is high because of the local topography and geochemical effects that lead to the high level of high degree of terrestrial radiation (Quindos et al., 1994). Some regions in the world, such as Guarapari in Brazil, Kerala in India, Ramsar in Iran, and Yangjiang in China (Hendry et al., 2009) and few other counties (Ghiassi-Nejad et al., 2002) are among the high background radiation areas in the world.

2.4 Heavy Metals in Soil

The existence of heavy metals in soil is due to the pedogenetic courses of endurance of parent materials at a degree that viewed as trace (<1000 $mg\,kg^{-1}$) and are sometimes toxic (Pierzynski et al., 2005). Following are the various parts of metals that exist in a soil: the soluble metal in the soil solution, metal-precipitates, metal absorbed to clays, hydrous oxides and organic matter, and metals within the matrix of soil minerals (Ashok et al., 2010). Majority of the soil from rural and urban areas may have one or more of the aforementioned heavy metals that have high background radiation, which can be hazardous to vegetation, animals and human health. This is because of the aggravation and increasing velocity of nature's gradually happening geochemical cycle of metals by man (D'amore et al., 2005).

Heavy metals and metalloids contaminate soil. These elements are radiated from the: fast growing industrial territories, mine tailings, removal of high metal wastes, leaded gasoline and paints, land usage of fertilizers, sewage sludge, pesticides, wastewater irrigation, spillage of petrochemicals, and coal combustion residues (Rahman et al., 2013).

2.5 Natural Radioactivity in Water

It is crucial to save water from contamination as water resources, especially surface water of rivers fulfils the requirement of humans, animals and industries. Rivers are beneficial to human in several ways such as, supply for irrigation, application for entertainment, sports activities, like water sports and fishing and above all it is a basic need of a human as drinking water (Shanbehzadeh et al., 2014). Many components like microorganisms, gases, radioactive particles, heavy metals, inorganic and organic materials may exist in the surface water. For this purpose, scientists will evaluate the quality of water by determining the quantity of components present in it (Hem, 1985).

The radionuclides in drinking water are members of natural radioactive series. These radionuclides are hazardous to the health of humans when they are either consumed by drinking water or are inhaled with during the domestic use (Cothern, 1990). In most surface water systems, uranium is present in dissolution while the presence of thorium in natural waters is pretty insoluble (Poschl and Nollet, 2006). Comparatively, the occurrence of thorium in earth's crust is 3 - 4 times more than that of uranium but it is rarely present in water because of its insolubility. However, due to the high radiotoxicity, ^{228}Ra being a part of ^{232}Th series may play a major role in contamination (Nuccetelli et al., 2012).